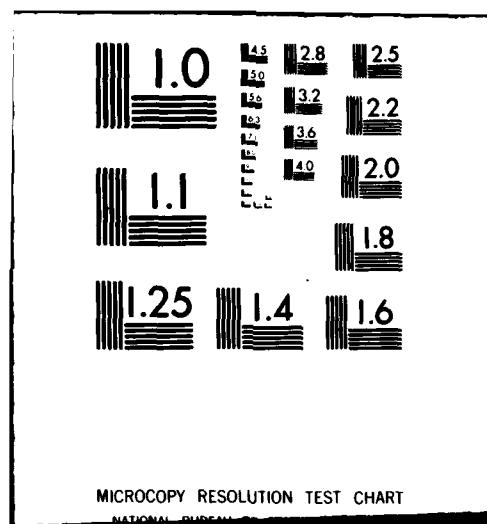


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**37** 20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Utilizing the technique of flash photolysis-resonance fluorescence the rate constants for the reactions of hydroxyl radicals (OH) with deuterium, hydrogen chloride, and propane were measured at elevated temperatures as high as 1000K. Distinct curvature was observed in the Arrhenius plots for OH reactions with HCl and propane while the OH + D<sub>2</sub> reaction rate coefficient seemed to follow the Arrhenius law quite well. The measured rate constants were compared with previous measurements in the literature.

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**THE KINETICS AND SPECTROSCOPY OF  
AIRCRAFT AND ROCKET PLUME CONSTITUENTS**

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**By:**

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Georgia Institute of Technology  
Atlanta, Georgia 30332**

**Co-Principal Investigators**

**Dr. A. R. Ravishankara      Dr. F. P. Tully**

**August 30, 1980**

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## ABSTRACT

During the past year progress has been made toward the dual objectives of this program: 1) to measure absolute rate constant temperature dependences for radical-molecule reactions of specific importance to modelling of combustion and plume processes in aircraft and rockets; and 2) to contribute to the general understanding of the temperature dependence of bimolecular reactions, particularly as related to observed curvature in Arrhenius plots. Improved sensitivity in the flash photolysis-resonance fluorescence technique was achieved and high-accuracy rate constant measurements were made in the heretofore only marginally accessible 500-1000 K temperature regime. Kinetic data for the important reactions OH + D<sub>2</sub>, HCl, and C<sub>3</sub>H<sub>8</sub> was obtained.

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## INTRODUCTION

Aircraft and rocket exhaust plumes provide an energetic, highly non-uniform, local environment within which microscopic physical and chemical processes act to dictate the nature of bulk observations of the medium. Analyses of fuel performance and tracking procedures rely on modelling of those contributing processes which, in combination, govern the efficiency of the propulsion system or surveillance method under examination. Chemically, reactions within the combustor and afterburning within the plume place heavy demands on the estimating prowess of kinetic modellers. In most cases, it is simply not possible to calculate which among the myriad of possible processes are most important (and thus which among the possible molecular species are of greatest concern). Therefore, an extensive data base, promoting realistic modelling parameter limitations, is needed. From a kinetic standpoint, optimized acquisition of this data base implies the measurement of oxidant/fuel/reaction intermediate reaction rate constants needed directly for model input and/or required as bases for the generation of 'global' kinetic equations applicable to entire families of chemical reactions. Improvement of the understanding of those factors which govern the temperature dependence of combustor/plume relevant bimolecular reactions is the primary goal of this research program.

## PROGRESS SUMMARY

Historically speaking, our modern view of the temperature dependence of the rate constant for bimolecular gas-phase reactions originated with Arrhenius' model in 1889 [1]. Arrhenius' postulated equation,  $k(T) = A \exp(-E_a/RT)$ , endured as law into the 1960's. The development of improved experimental techniques applicable over extended temperature ranges of measurement

then spawned a large number of intercomparable studies and led to the initial clear case of failure of the simple Arrhenius' equation. Even up through the past few years, however, such failures were typically characterized merely by noting, for a particular reaction, substantial disagreement between the  $\log k(T)$  vs.  $1/T$  slopes obtained as the high-temperature ( $T > 1000K$ ) and low-temperature ( $T < 500K$ ) straight-line extrapolations. It has not been, in the past decade, that curvature in the  $\log k(T)$  vs.  $1/T$  (so-called Arrhenius) plot is unacceptable; theoretically, curvature has been considered likely for some time. The lack of sufficient congruence of data in either (high or low) temperature regime and the nearly total absence of reliable rate constant data between 500K and 1000K has delayed until quite recently and limited to just a very few reactions even the empirical smooth joining of high and low temperature measurements.

It is precisely that void in elementary reaction rate constant measurements from 500-1000 K that has inspired the development and growth of this research program. Using our technique, we can obtain data in the intermediate temperature range, and also completely cover the low temperature regime of 220-500 K, thus providing one set of data which spans nearly a factor of five in  $1/T$  values. During the second year of the program, rate coefficient measurements over extended temperature ranges, were made for the following reactions:



Distinct curvature in the Arrhenius plot, varying in degree, was found for each Reaction (1)-(4) [2].

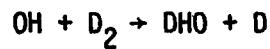
During the past year, this work has been expended to the following reactions:



Again, distinct curvature in the Arrhenius plot has been observed for Reactions (6) and (7). Surprisingly, Reaction (5) seems to follow a nearly linear Arrhenius plot in the temperature range of 298-1000 K. Our results for Reaction (5) are listed in Table I and are plotted in Figure 1. Also shown in Figure 1 are the results of Smith and Zellner [3], the single reported study of Reaction (5); in this investigation covered a temperature range of 220-460 K. Our lower temperature results agree quite well with Smith and Zellner's data the temperature range overlapped by the two studies. Extrapolation of Smith and Zellner's data to 1000K gives a value of  $k_5$  which is approximately 60% lower than our data suggests; this clearly is due to the slight curvature in the Arrhenius plot for Reaction (5).

Figure 2 shows Arrhenius plots for Reactions (1) and (5). It is clear from the plots that the Arrhenius plot for Reaction (5) is reasonably straight while that for Reaction (1) is curved! The explanation for this observation may be that H-atom tunneling is more pronounced in Reaction (1) than that of D-atom in (2). Alternatively, it may be due to the mass effect in the transition state complex. To better answer this question, we have extended the measurement of both  $k_1$  and  $k_5$  to lower temperatures, i.e.,  $\sim 230\text{K}$ . The data

Table I.



<u>Temperature (K)</u>	<u><math>k</math> bimolecular<sup>*</sup> <math>\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}</math></u>
298	$(2.00 \pm 0.17) \times 10^{-15}$
380	$(1.16 \pm 0.13) \times 10^{-14}$
438	$(3.07 \pm 0.23) \times 10^{-14}$
449	$(3.35 \pm 0.14) \times 10^{-14}$
471	$(4.81 \pm 0.37) \times 10^{-14}$
525	$(8.86 \pm 0.85) \times 10^{-14}$
572	$(1.84 \pm 0.06) \times 10^{-13}$
617	$(2.31 \pm 0.04) \times 10^{-13}$
752	$(5.21 \pm 0.19) \times 10^{-13}$
788	$(5.93 \pm 0.34) \times 10^{-13}$
824	$(7.8 \pm 1.1) \times 10^{-13}$
932	$(1.11 \pm 0.05) \times 10^{-12}$

<sup>\*</sup>Stated error limits are  $2\sigma$  values and refer to the precision of the experiment.

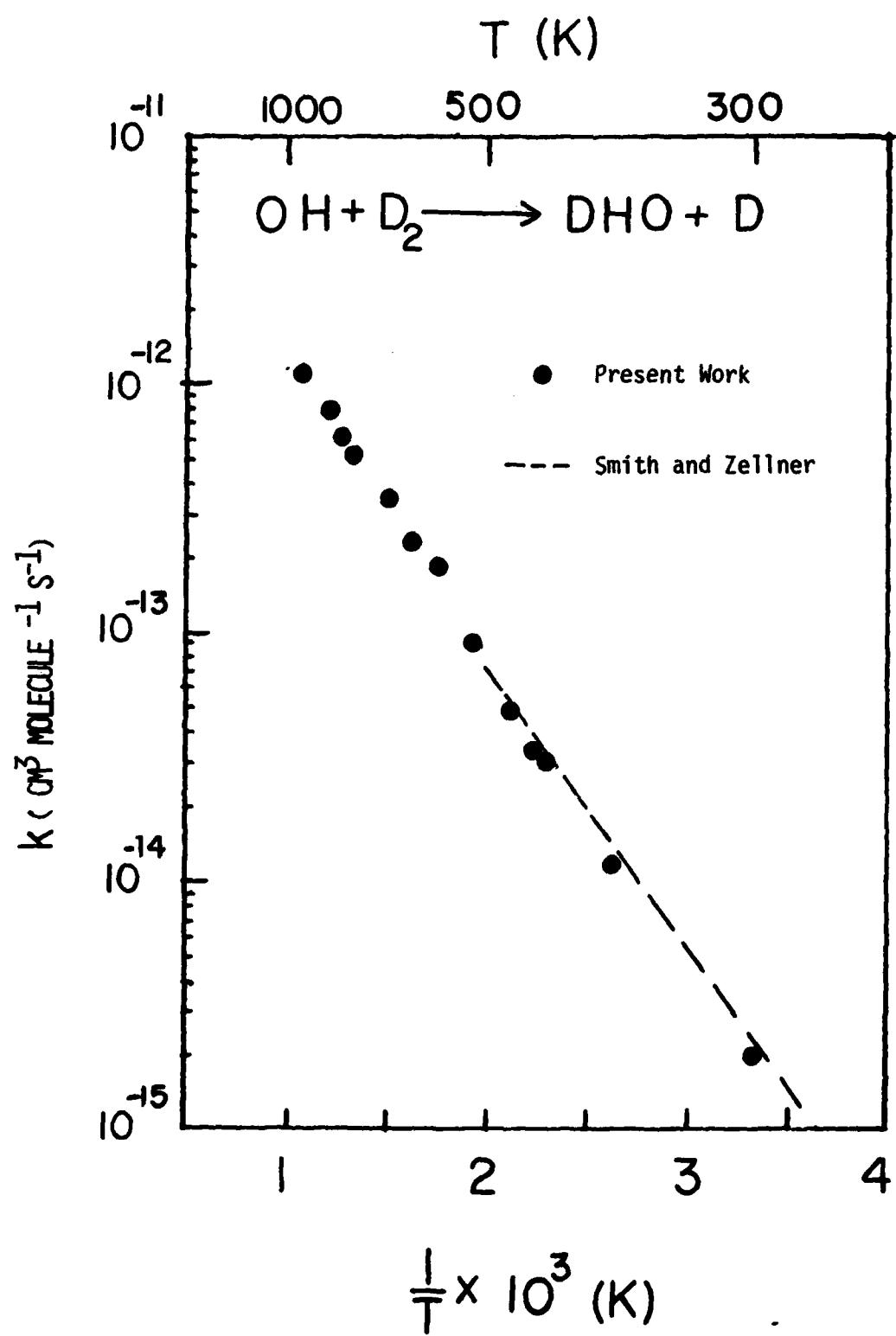


Figure 1.

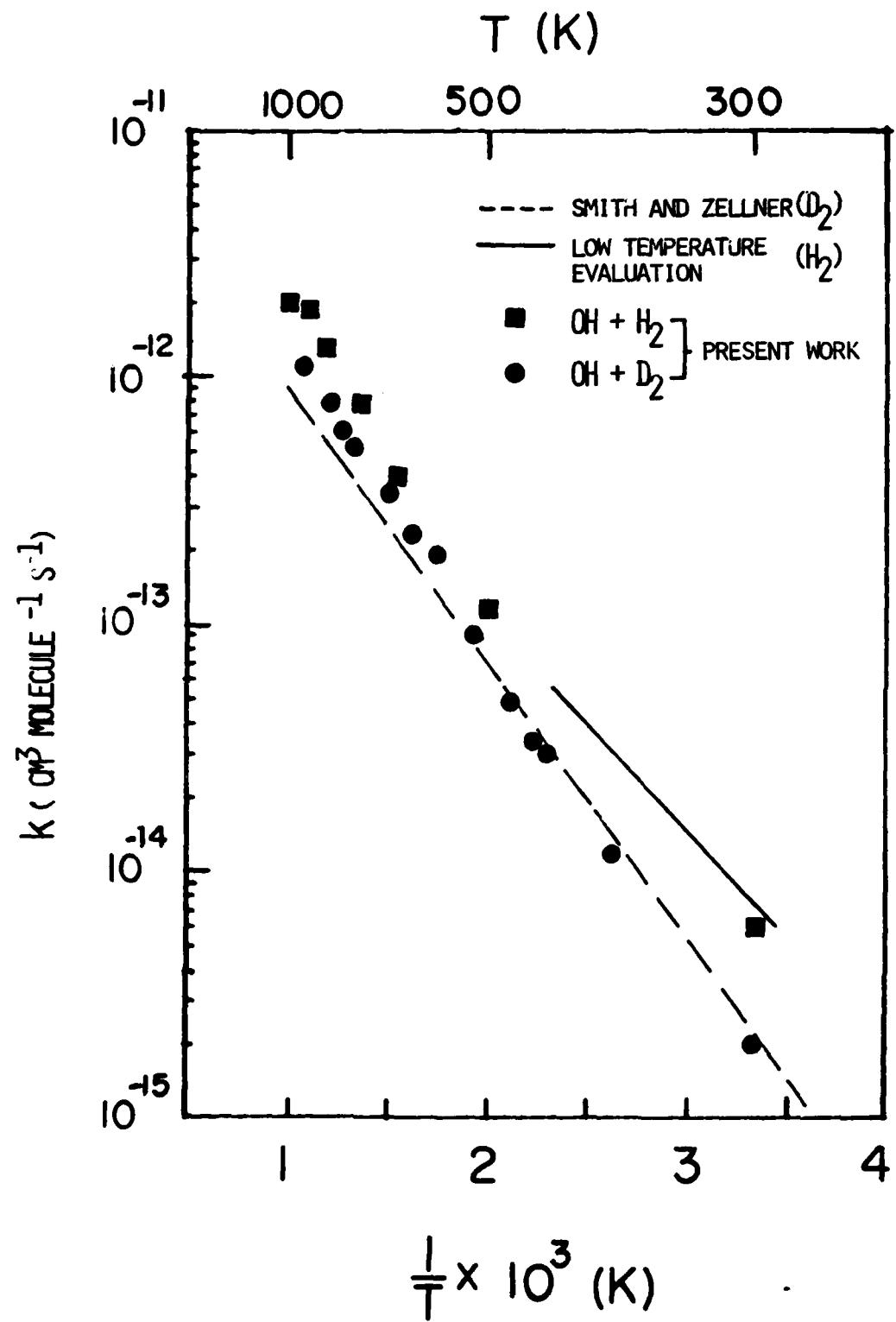


Figure 2.

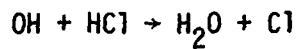
analysis is currently underway and we should have the results in the next few weeks.

Absolute reaction rate coefficient measurements obtained for Reaction (6) are listed in Table II and are plotted in Figure 3. Also shown are the results of three low temperature investigations [3,4,5] of Reaction (6). It is clear that the low temperature results do not extrapolate well to high temperatures. Even the results of Smith and Zellner [3], which gave the largest activation energy, fall below our results. Of course, it should be noted, that our low temperature results are in excellent agreement with all three previous measurements. This curved Arrhenius plot for Reaction (6) suggests that HCl would react with OH faster (by ~ a factor of 2) at plume temperatures.

Experimental measurements of  $k_7(T)$  for Reaction (7) are listed in Table III and plotted in Figure 4. Prior to these measurements, the only reliable rate coefficients existing for this reaction were a few measurements at and slightly above room temperature. Once again, it can be seen from Figure 4 that straight-line extrapolation of low temperature measurements [6] results in an underestimation of the bimolecular rate constant  $k_7(T)$  at higher temperatures; concave upward curvature is again evident.

The value of these results (and of our developed experimental technique) is not limited to the numerical achievements detailed above. Typically, the complexity of the chemistry involved in a combustion and/or plume process is nearly overwhelming. In recent years it has become increasingly obvious that it is simply not possible to measure the kinetic parameters for all contributing elementary reactions in a complex process. Indeed, if such a data base did exist, computational limitations would prevent its full utilization. Increasing attention is thus being focused on the generation of 'global' kinetic

Table II.



<u>Temperature (K)</u>	<u><math>k</math> bimolecular*</u> <u><math>\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}</math></u>
273	$(6.56 \pm 0.98) \times 10^{-13}$
298	$(6.89 \pm 0.60) \times 10^{-13}$
350	$(8.50 \pm 0.59) \times 10^{-13}$
402	$(9.9 \pm 1.0) \times 10^{-12}$
416	$(1.09 \pm 0.10) \times 10^{-12}$
454	$(1.15 \pm 0.06) \times 10^{-12}$
500	$(1.23 \pm 0.17) \times 10^{-12}$
617	$(1.88 \pm 0.06) \times 10^{-12}$
752	$(2.48 \pm 0.27) \times 10^{-12}$
824	$(2.69 \pm 0.38) \times 10^{-12}$
932	$(3.63 \pm 0.46) \times 10^{-12}$
1000	$(4.14 \pm 0.37) \times 10^{-12}$

\* Stated error limits are  $2\sigma$  values and refer to the precision of the experiments.

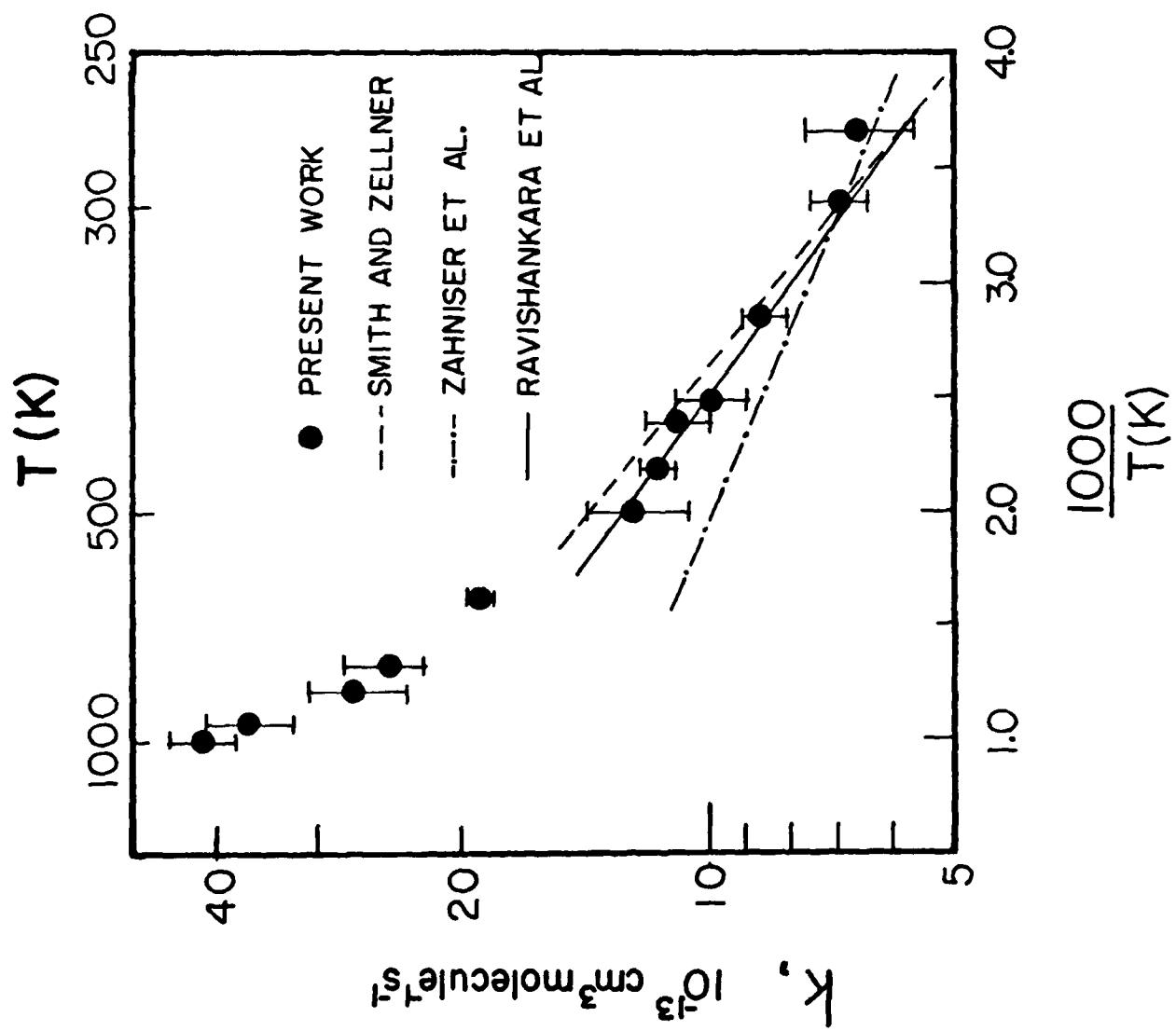
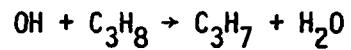


Figure 3.

Table III.



<u>Temperature (K)</u>	<u><math>k</math> bimolecular*</u> <u><math>\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}</math></u>
298	(1.05 0.04) $\times 10^{-12}$
326	(1.48 0.06) $\times 10^{-12}$
378	(2.51 0.20) $\times 10^{-12}$
469	(3.37 0.23) $\times 10^{-12}$
554	(4.78 0.34) $\times 10^{-12}$
690	(8.78 0.97) $\times 10^{-12}$

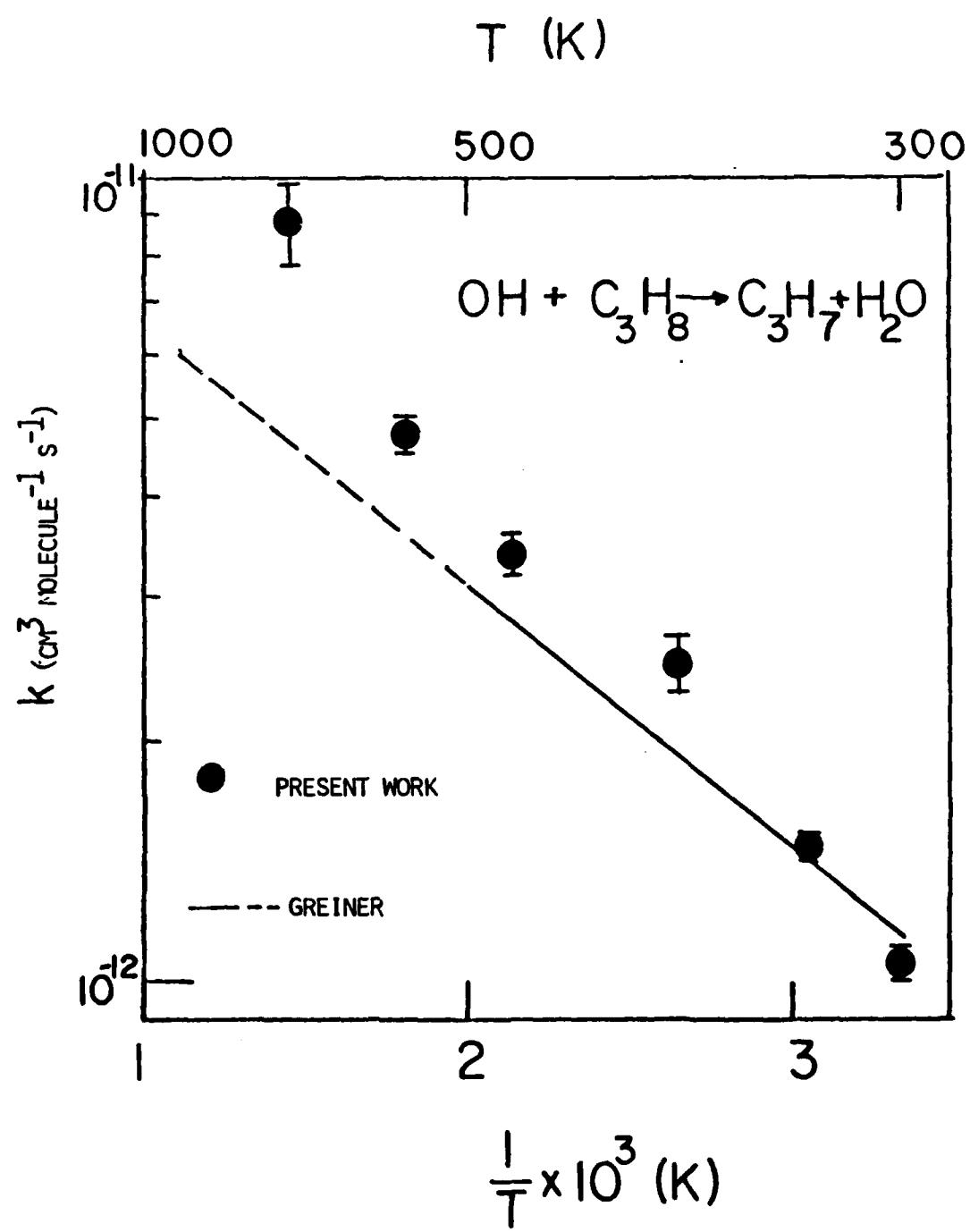


Figure 4.

equations, i.e., kinetic expressions which are approximately applicable to families of analogous chemical reactions. Such a viewpoint then argues the need for investigations which emphasize the effects of chemical structure on the rates of reactivity; studies aimed at generating an improved understanding of the general temperature dependence of bimolecular reaction rates must be pursued. The results obtained in this program should be considered to represent some of the initial steps of this approach.

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## PUBLICATIONS

1. "A Flash Photolysis-Resonance Fluorescence Kinetic Study of the Reaction  $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{M}$  and  $\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \text{CH}_3$  from 298-1020 K," F. P. Tully and A. R. Ravishankara, *J. Phys. Chem.*, in press.
2. "A Flash Photolysis-Resonance Fluorescence Kinetic Study of the Reaction of  $\text{OH} + \text{O}_2 \rightarrow \text{DHO} + \text{H}$  from 230-1000 K," A. R. Ravishankara, R. C. Shah, J. M. Nicovich, R. L. Thompson, and F. P. Tully, *J. Phys. Chem.*, to be submitted.

## PERSONNEL

Although many of these experiments have been performed by the Co-principal Investigators, other personnel have made significant contributions to the execution of this program. In particular,

J. M. Nicovich — Research Scientist I

R. L. Thompson — Cooperative Division Student

have benefited the program.